Fluorescent Quantum Dots for Sensing Applications

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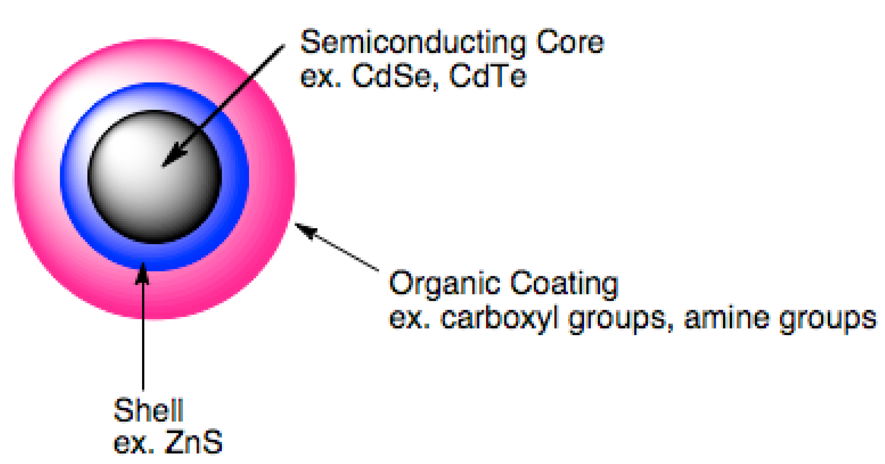
Abstract: We have explored the preparation of specifically modified fluorescent quantum dots for various sensing applications. A variety of quantum dot core and shell combinations were investigated and several different strategies for surface modification were applied. Preliminary results with quantum dots modified with boronic acids show a modest increase in fluorescence intensity as concentration of ethylene glycol is increased. With further modifications we hope to achieve improved brightness, solubility, and analyte sensitivity.

Background:

Quantum dots (QDs) are nanometer-sized crystals composed of semiconducting materials such as CdSe or ZnS. The optical properties of these fluorescent nanomaterials can be tuned by careful control of QD size and surface chemistry. Interest in fluorescent QDs derives from their broad absorption, narrow emission, intense brightness, and good photostability relative to organic dyes. Widely used in a variety of applications, QDs truly constitute a unique class of nanomaterials. Often, additional coatings of materials such as ZnS or silica are added to provide improved photostabilty and to provide a scaffold for the installation of additional functional groups at the surface.



Significantly, because they are so small, the optical properties of QDs are quite sensitive to changes in the surface chemistry that occur when new molecules or ions bind to the surface. This sensitivity makes them excellent candidates as fluorescent sensors. To achieve a specific sensitivity to a particular analyte, we are investigating with the attachment of particular ligands with specific attractions for different analytes.

Experimental Methods:

General:

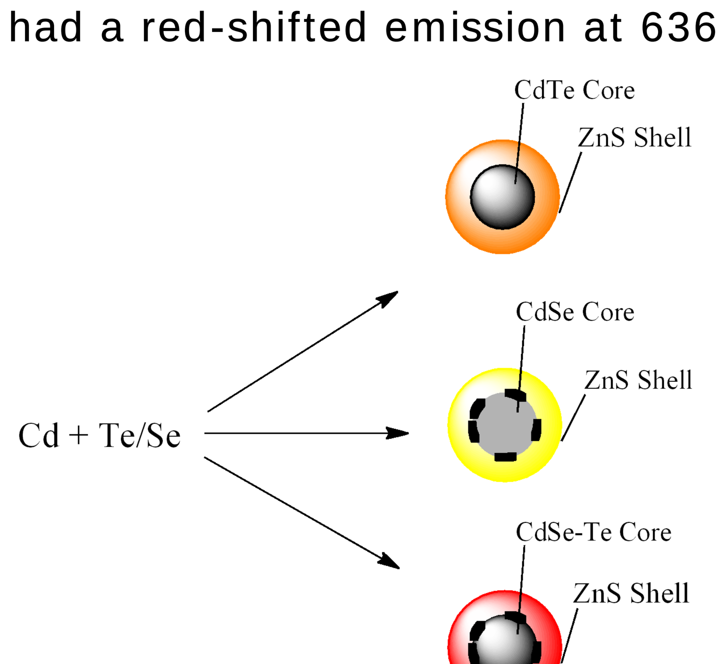
Previously, we had used the method depicted in Scheme 1 to prepare ZnS-Mn^{2+} doped QDs. The QDs used in our current research consist of a CdTe core coated with a two-layer ZnS shell as shown in Scheme 2. Using coordinating solvents such as trioctylphosphine (TOP) or tetradecylphosphonic acid (TDPA), a tellurium precursor was heated to high temperature and transferred to a hot Cd solution. When combined, the CdTe solution became increasingly bright red in color. QD samples with different sizes and optical properties could be obtained by removal at different times after the addition. Next a ZnS precursor was added to the CdTe solution to provide a ZnS shell.

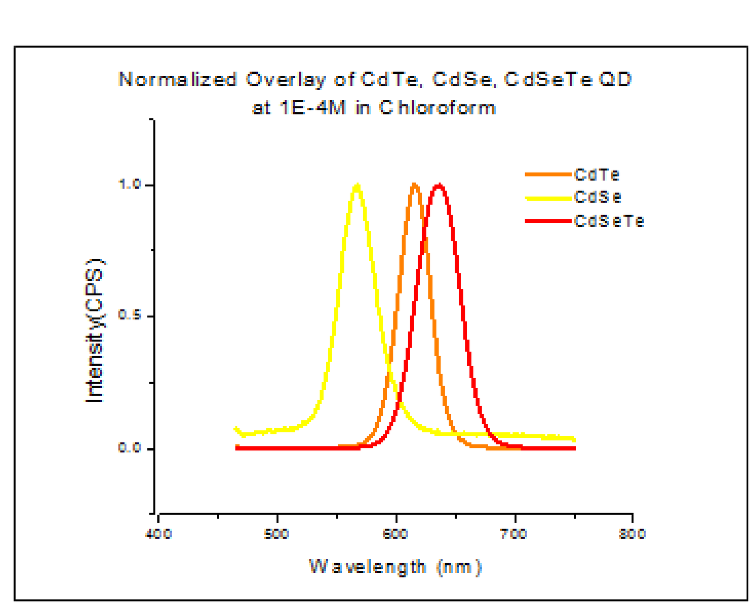
Scheme 1:

Scheme 2:

Core Modification:

Although our research focused on using CdTe as the core material, two other cores were examined for fluorescence properties. CdSe and a CdTeSe mix were evaluated against CdTe. To synthesize these QDs the same method was used, the difference being the precursor (either Te, Se, or TeSe depending) that were transferred into the Cd solution. Fluorescence spectra were recorded for all three cores (Figure 1). The CdTe QDs had a wavelength at 616 nm while those composed of CdSe had a more blue-shifted emission as 568 nm. Lastly, the mixed CdTeSe had a red-shifted emission at 636 nm.





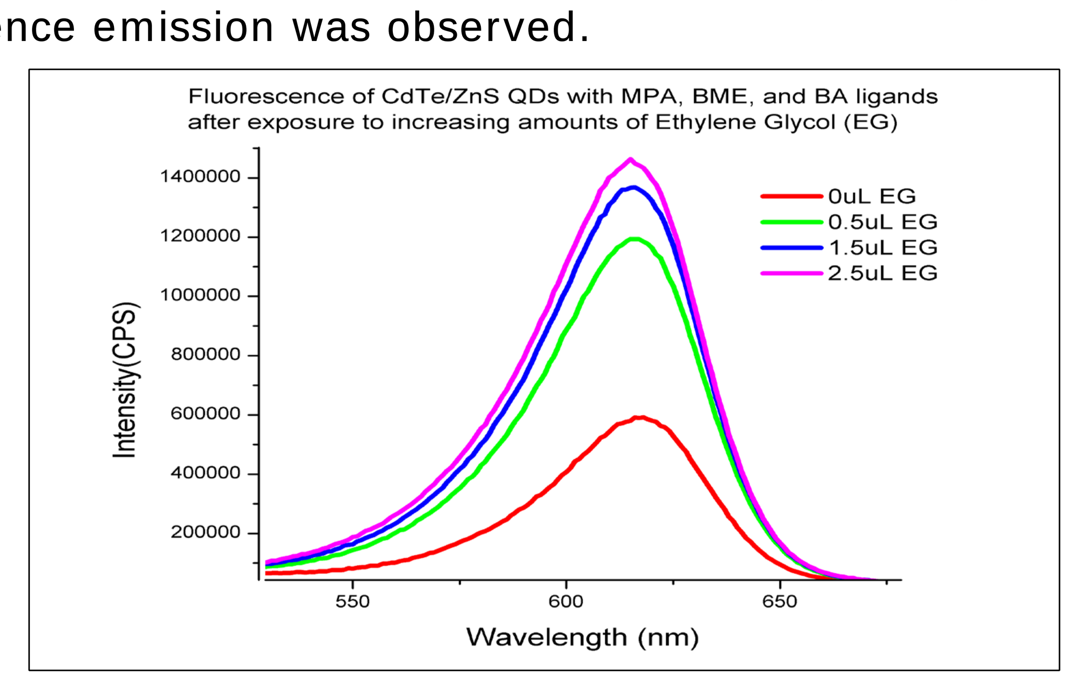
MPA:

Having QDs that are soluble in water is a highly valued characteristic. In order to make the CdTe/ZnS QDs water-soluble, mercaptopropionic acid (MPA) was bound to the ZnS shell through a disulfide bond, replacing the hydrophobic surfactants (TOP and TDPA). This was achieved by adding the hydrophobic QDs to an MPA/methanol solution under basic conditions.

Boronic Acid Modification:

We were able to functionalize the CdTe/ZnS quantum dots with mercaptoboronic acid. Boronic acid is a common sugar-sensing molecule as it easily binds to sugars. We were able to attach this to the quantum dots by using a disulfide bond to the ZnS shell. By using various ratios of mercaptoboronic acid to MPA to beta-mercaptoethanol (BME) we were able to obtain functionalized quantum dots that were still soluble in aqueous solution. The MPA and BME were used to make the quantum dots soluble once the mercaptoboronic acid was added.

When the functionalized QDs were exposed to ethylene glycol a change in fluorescence emission was observed.



Silica Modification:

Based on a procedure from Qian *et al.*, we modified CdTe/ZnS QDs by way of a microemulsification. This synthesis encapsulates the QDs in a silica shell with attached carboxyl groups for the purpose of improving QD water-solubility and photostability.

Future Work:

- Optimize the quantum dots with the silica shell.
- Functionalize the CdTeZnS/Silica quantum dots with boronic acid for sugar sensing
- Functionalize the CdTeZnS/Silica quantum dots with 8-hydroxyquinoline for metal sensing

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